FORM PTO-1390 (REV. 11-94)

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER
2988-679

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

09/869207

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR99/02786	November 12, 1999	December 22, 1998

TITLE OF INVENTION
PROCESS FOR MANUFACTURING HYDRAZINE BY HYDROLYSING AN AZINE

APPLICANT(S) FOR DO/EO/US
George BRENGUER, Jean-Philippe RICARD, and Michel VIDAL

Applicant herewith submits to the United States Designated/ Elected Office (DO/EO/US) the following items under 35 U.S.C. 371:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the international Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)

6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureaus.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 37(c)(3)).

9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☒ Other items or information:
    International Publication WO 00/37357 with International Search Report
    Form PCT/IB/306
    International Preliminary Examination Report (in French)

NY2 - 1210768.1

EXPRESS MAIL NO.: EL 501 640 370 US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: Brenguer et al.	Group Art Unit: To be assigned
Serial No.: to be assigned	Examiner: To be assigned
Filed: Concurrently filed	Attorney Docket No.: 2988-679
For: PROCESS FOR MANUFACTURING HYDRAZINE BY HYDROLYSING AN AZINE	New York, NY June 22, 2001

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Applicant respectfully requests entry of the following amendment and remarks in to the file of the above identified application. Marked up versions of all revised claims, showing insertions, which are underlined, and deletions, which are bracketed, are included in Appendix A. Amendments are shown in bold-face for convenience of reference. Applicants also have attached a list of all pending claims after amendment in clean form as Appendix B.

IN THE CLAIMS:

Please amend claims as follows:

1. (Once amended) A process for manufacturing hydrazine comprising
providing a distillation column having a boiling vessel
feeding azine and water to the top of the distillation column;
heating the azine and water in the column to hydrolyze the azine to produce hydrazine and ketone;
removing the hydrazine at a bottom of the column; and
removing the ketone at the top of the column,

wherein heat required for the hydrolyzing step and the removing steps is supplied by the boiling vessel and by injection of vaporized water into the column.

2. (Once amended) The process according to Claim 1, characterized in that the vaporized water is injected into the bottom of the column.

3. (Once amended) The process according to claim 1, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % by weight of the total water.

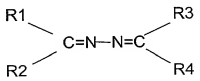
4. (Once amended) The process according to claim 1, characterized in that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

Please add the following new claims:

5. (New) The process according to claim 1, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

6. (New) The process according to claim 1, wherein the vaporized water is injected into the column at two or more points of the column.

7. (New) The process according to claim 1, wherein the azine has the following formula:



wherein R1 to R4 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R1 and R2 and/or R3 and R4 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected to nitrogen atom, R1 to R4 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

8. (New) The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

9. (New) A process for manufacturing hydrazine, which comprises

feeding a distillation column having a boiling vessel with hydrazone and water at a top of the column;

heating the hydrazone and water in the column to hydrolyze the hydrazone to produce hydrazine and ketone;

removing the hydrazine at a bottom of the column; and

removing the ketone at the top of the column,

wherein heat required for the hydrolyzing step and the removing steps is supplied by the boiling vessel and by injection of vaporized water into the column.

10. (New) The process 9 according to Claim 9, characterized in that the vaporized water is injected into the bottom of the column.

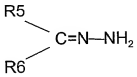
11. (New) The process according to claim 9, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % by weight of the total water.

12. (New) The process according to claim 9, characterized in that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

13. (New) The process according to claim 9, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

14. (New) The process according to claim 9, wherein the vaporized water is injected into the column at two or more points of the column.

15. (New) The process according to claim 9, wherein the hydrazone has the following formula:



wherein R5 and R6 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R5 and R6 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected to nitrogen atom, R5 and R6 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

16. (New) The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

REMARKS

Claims 1-16 are in the case. Claims 1-4 have been amended to particularly point out and distinctly claim the invention and to avoid multiply dependent claims without narrowing the scope of claims. Claims 5-16 have been added. Supports for the amendment and newly added claims can be found in the entire specification and claims as originally filed, e.g., supports for claim 5 can be found in claim 3 before amendment and specification page 5, lines 11-13, for claim 6, on page 6, lines 1-4, for claims 7 and 8, on page 6, line 27 to page 7, line 12, for claims 9-12, in claim 1-4 before amendment, for claim 13, on page 5, lines 11-13, for claim 14, on page 6, lines 1-4, for claims 15-16, on page 6, line 27 to page 7, line 12. No new matter is believed to be introduced.

No fee, other than that for the extension of time, is believed due for the filing of this response. Should any fees be required, however, please charge such fees to Pennie & Edmonds LLP Deposit Account No. 16-1150.

Respectfully submitted,

mail to (Limited Recognition)
for Charles Miller

Date: June 22, 2001

24,576
Charles E. Miller (Reg. No.)

PENNIE & EDMONDS LLP
1155 Avenue of the Americas
New York, New York 10036-2711
(212) 790-9090

Attorneys For Applicant

APPENDIX A

1. (Once amended) A process **[Process]** for manufacturing hydrazine **[by hydrolysing an azine, which is carried out in a column]** **comprising**

providing a distillation column having a boiling vessel

[fed at the top] **feeding** **[with]** azine and water **[,]** **to the top of the distillation column;**

heating the azine and water in the column to hydrolyze the azine to produce hydrazine and ketone;

[and from which] **removing the** hydrazine **[is removed]** at **[the]** **a** bottom **of the column;** and

removing the ketone **[released is removed]** at the top **of the column**, **[characterized in that the]** **wherein** heat required for the **[reactions]** **hydrolyzing step** and the **[separation of the various components]** **removing steps** is **[partly]** supplied by **[means of a]** **the** boiling vessel and **[partly]** by injection **[, into at least one point of the column,]** of vaporized water **into the column**.

2. (Once amended) **The process** **[Process]** according to Claim 1, characterized in that the vaporized water **is** injected into the bottom of the column.

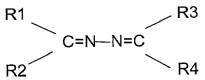
3. (Once amended) **The process** **[Process]** according to **[either of claims 1 and 2]** **claim 1**, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % **by weight** **[and preferably from 40 to 60 %]** of the total water.

4. (Once amended) **The process** **[Process]** according to **[one of Claims 1 to 3]** **claim 1**, characterized **in** that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

5. (New) The process according to claim 1, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

6. (New) The process according to claim 1, wherein the vaporized water is injected into the column at two or more points of the column.

7. (New) The process according to claim 1, wherein the azine has the following formula:



wherein R1 to R4 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R1 and R2 and/or R3 and R4 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected to nitrogen atom, R1 to R4 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

8. (New) The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

9. (New) A process for manufacturing hydrazine, which comprises feeding a distillation column having a boiling vessel with hydrazone and water at a top of the column;

heating the hydrazone and water in the column to hydrolyze the hydrazone to produce hydrazine and ketone;

removing the hydrazine at a bottom of the column; and

removing the ketone at the top of the column,

wherein heat required for the hydrolyzing step and the removing steps is supplied by the boiling vessel and by injection of vaporized water into the column.

10. (New) The process 9 according to Claim 9, characterized in that the vaporized water is injected into the bottom of the column.

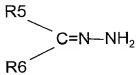
11. (New) The process according to claim 9, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % by weight of the total water.

12. (New) The process according to claim 9, characterized in that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

13. (New) The process according to claim 9, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

14. (New) The process according to claim 9, wherein the vaporized water is injected into the column at two or more points of the column.

15. (New) The process according to claim 9, wherein the hydrazone has the following formula:



wherein R5 and R6 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R5 and R6 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected to nitrogen atom, R5 and R6 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

16. (New) The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

APPENDIX B

1. A process for manufacturing hydrazine comprising
providing a distillation column having a boiling vessel
feeding azine and water to the top of the distillation column;
heating the azine and water in the column to hydrolyze the azine to produce hydrazine and ketone;
removing the hydrazine at a bottom of the column; and
removing the ketone at the top of the column,
wherein heat required for the hydrolyzing step and the removing steps is supplied by the boiling vessel and by injection of vaporized water into the column.

2. The process according to Claim 1, characterized in that the vaporized water is injected into the bottom of the column.

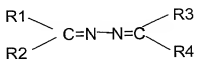
3. The process according to claim 1, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % by weight of the total water.

4. The process according to claim 1, characterized in that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

5. The process according to claim 1, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

6. The process according to claim 1, wherein the vaporized water is injected into the column at two or more points of the column.

7. The process according to claim 1, wherein the azine has the following formula:



wherein R1 to R4 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R1 and R2 and/or R3 and R4 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected

to nitrogen atom, R1 to R4 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

8. The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

9. (New) A process for manufacturing hydrazine, which comprises feeding a distillation column having a boiling vessel with hydrazone and water at a top of the column;
heating the hydrazone and water in the column to hydrolyze the hydrazone to produce hydrazine and ketone;
removing the hydrazine at a bottom of the column; and
removing the ketone at the top of the column,
wherein heat required for the hydrolyzing step and the removing steps is supplied by the boiling vessel and by injection of vaporized water into the column.

10. The process 9 according to Claim 9, characterized in that the vaporized water is injected into the bottom of the column.

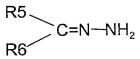
11. The process according to claim 9, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % by weight of the total water.

12. The process according to claim 9, characterized in that the vaporized water is at a temperature of between 130 and 220 °C and at relative pressure of between 3 and 18 bar.

13. The process according to claim 9, wherein the amount of water injected in the form of vaporized water represents from 40 to 60 % of the total water.

14. The process according to claim 9, wherein the vaporized water is injected into the column at two or more points of the column.

15. The process according to claim 9, wherein the hydrazone has the following formula:



wherein R5 and R6 are identical or different and are hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, R5 and R6 may connect to each other and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms which constitutes a cycle containing from 4 to 13 carbon atoms including the carbon atom directly connected to nitrogen atom, R5

and R6 may be substituted with chlorine, bromine, fluorine, or nitro, hydroxy or alkoxy group or an ester function.

16. The process according to claim 7, wherein the azine is acetone azine or methyl ethyl ketazine.

PATENT APPLICATION	
COUNTRY:	France
No.:	98 16257
FILED ON:	22 December 1998
FILE:	AM 1404

ABSTRACT

PROCESS FOR MANUFACTURING HYDRAZINE BY HYDROLYSING AN AZINE

Company known as : ELF ATOCHEM S.A.
4/8 Cours Michelet
La Défense 10
92800 PUTEAUX

Authorized agent : Pierre GRANET

Inventors : Jean Philippe RICARD
Georges BRENGUER
Michel VIDAL

The invention relates to a process for manufacturing hydrazine by hydrolysing an azine, in which the heat required for the reaction and the separation by distillation of the components is partly provided by injecting vaporized water.

PROCESS FOR MANUFACTURING HYDRAZINE BY HYDROLYSING AN AZINE

DESCRIPTION

The present invention relates to an improved process for manufacturing hydrazine by hydrolysing an azine.

The industrial production of hydrazine is carried out according to the Raschig, Bayer or Atochem processes.

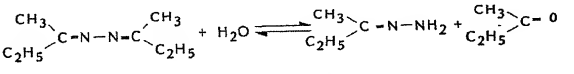
In the Raschig process, ammonia is oxidized with a hypochlorite to obtain a dilute hydrazine solution which must then be concentrated by distillation.

The Bayer process is a variant of the Raschig process, which consists in displacing a chemical equilibrium by trapping, using acetone, the hydrazine formed in the form of azine $(CH_3)_2C = N-N = C(CH_3)_2$. The azine is then isolated, after which it is hydrolysed to hydrazine.

The Atochem process consists in oxidizing a mixture of ammonia and methyl ethyl ketone with hydrogen peroxide in the presence of a catalyst to prepare the azine directly, which then simply requires hydrolysis to hydrazine. The Atochem process is described in many patents, for example US patents 3,972,878, 3,972,876, 3,948,902 and 4,093,656.

The hydrolysis of an azine into hydrazine is described in the Schirmann et al., US patents 4,724,133 and 4,725,421 and in GB patent 1,164,460.

This hydrolysis is carried out according to the standard reaction model, which makes it possible to go successively from the azine (I) to the corresponding hydrazone (II), and then from the hydrazone (II) to the hydrazine (III). For example, in the case of methyl ethyl ketone :



(I) (II)

(II) (III)

Since these two reactions are equilibrated, the equilibrium being very greatly displaced to the left, it is necessary to work under distilling conditions in order to remove the reaction products if it is desired to obtain hydrazine free of ketone.

This hydrolysis is thus carried out in a distillation column, the size of which is sufficient for it to be possible to install the two reaction zones as well as the depletion functions as regards the bottom of the column, and the concentration functions as regards the top of the column.

In practice, the column is fed with azine and water at the top. These hydrolysis reactions take place at a speed which is compatible with correct functioning of an industrial plant, only within a temperature range of greater than 140°C and limited at the top to 185-190°C on account of the instability of hydrazine at higher temperatures.

The two reactions described above are endothermic and it is necessary to supply the system with heat both for the reaction system and for maintaining the distilling conditions.

The principle of the distillation columns is based on the fact that, in general, all of the energy needs are supplied by means of a boiling vessel placed at the bottom of the column, which can be heated by various means, such as superheated steam, oil, heating fluid or electrical heating.

The Applicant has already observed that if a heat-siphon boiling vessel with a coil submerged at the bottom of the column or a tubular array mounted parallel to the bottom of the column is used, a phenomenon of decomposition of the hydrazine associated with the high temperature of the metal wall is observed.

The Applicant has proposed, in European patent No. 0,431,998, a practical means for reducing this decomposition. It consists in particular in working with a forced-circulation boiling vessel and using either

titanium or chromium oxide as the material for the boiling vessel.

The Applicant has discovered that it is possible to further improve the yield for the process by minimizing the losses of hydrazine hydrate by decomposition, by means of using a boiling technique which is suited to the reaction and the components.

A subject of the invention is a process for manufacturing hydrazine by hydrolysing an azine, which is carried out in a column fed at the top with azine and water, and from which hydrazine is removed at the bottom and the ketone released is removed at the top, characterized in that the heat required for the reactions and the separation of the various components is partly supplied by means of a boiling vessel and partly by injection, into at least one point of the column, of vaporized water.

The decomposition of hydrazine at the bottom of the column takes place in the boiling vessel and occurs according to the following reactions :

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \text{ (I)}$$
$$2N_2H_4 \rightarrow N_2 + 2NH_3 + H_2 \text{ (II)}$$

Reaction (I) generally represents 95 % of the decomposition.

The proposed solution makes it possible to greatly minimize the losses of hydrazine by injecting, into the bottom of the column, some of the water required

to hydrolyse the azine, this water being in the form of vaporized water, which also supplies additional heat required for the separation by distillation. This makes it possible either to lower the temperature in the boiling vessel or to reduce the surface area and, in either case, to reduce the decomposition of the hydrazine.

The term "vaporized water" means water whose temperature is generally between 130 and 220°C and whose relative pressure is between 3 and 18 bar.

The water introduced in the form of vaporized water represents between 20 and 80 % and preferably between 40 and 60 % of the total water.

This water may originate either from an external feed or from a recycling of the process water originating from the other steps of the overall process.

The choice of the precise characteristics of this vaporized water, as well as the amount used, naturally depends on the reaction carried out and the operating conditions of the column.

The vaporized water is generally injected into a single point, for reasons of simplicity, and this point is preferably located at the bottom of the column, and advantageously in a region in which the ratio of the "point of injection - highest point of column" and "point of injection - lowest point of column" distances is greater than or equal to 5/1.

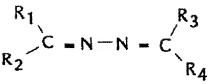
In one variant of the process, there may be two or more points of injection, one of them, the one supplying more than 50/60 % of the heat supplied in this form, being located at the bottom of the column.

The efficacy of the process is determined by the amount of hydrazine formed and decomposed, and this is done by measuring, at the column vents, the analytical composition of the effluent : nitrogen, ammonia, hydrogen. From this composition, the decomposition due to the reaction (I), volume of nitrogen, and to the reaction (II), volume of hydrogen, are deduced.

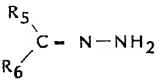
The process of the invention applies to a hydrolysis process using a conventional boiling vessel, by supplying heat at the bottom of the column. It is preferably used with the boiling method described in patent EP 0,431,998, in which, to heat the aqueous hydrazine solution essentially in liquid phase, the liquid phase is placed under pressure during the heating, i.e. the aqueous hydrazine solution absorbs heat energy in the form of an increase in its temperature, and this solution is then depressurized and the previous energy is yielded in the form of a vaporization, i.e. a forced-circulation boiling vessel is used.

The process of the invention applies to the hydrolysis of azines or homologous products such as hydrazone.

The terms "azine" and "hydrazone" respectively denote the products of formulae :



and



in which R_1 to R_6 are identical or different and denote hydrogen, a linear alkyl radical containing from 1 to 12 carbon atoms, a branched alkyl radical or a cycloalkyl radical containing from 3 to 12 carbon atoms, or an aryl radical containing from 6 to 12 carbon atoms. The radicals R_1 to R_6 connected to the same carbon atom of the azine or of the hydrazone can themselves be connected and can together represent a linear or branched alkylene radical containing from 3 to 12 carbon atoms.

All the above radicals R_1 to R_6 can also be substituted with a chlorine, a bromine, a fluorine or a nitro, hydroxyl or alkoxy group or an ester function. The invention is particularly useful for the acetone azine :

$$CH_3(CH_3)C = N—N = C(CH_3)CH_3$$

methyl ethyl ketazine

$$C_2H_5(CH_3)C = N—N = C(CH_3)C_2H_5$$

and the corresponding hydrazones.

Figure 1 describes a device for carrying out the process of the invention and Figure 2 describes a device therefor of the prior art.

In Figure 1, (1) represents a distillation column into which azine is introduced at the top of the column via the pipe (2) and water is introduced via the pipe (4). A fraction of the water supplied via the pipe (3) is sent via the pipe (5) to an exchanger (6) and then fed, in the form of vaporized water, into the bottom of the column (1). The hydrazine produced is removed from the bottom of the column via the pipe (7). A fraction of this hydrazine is deviated via the column and sent to a pump (9) and then to an exchanger (10) before being reinjected at a higher temperature into the bottom of the column (1). A ketone/water azeotrope and inert gases are removed from the top of the column (1) via the pipe (11) and are separated, after passage through an exchanger (12). The ketone/water azeotrope liquid fraction is partially recycled via the pipe (14) into the top of the column (1).

Figure 2 illustrates the technique of the prior art, in which the water is introduced into the top of the column (1) via the pipe (3). The hydrazine formed is removed via the pipe (7) and partially recycled into the column (1) via the pipe (8) after passage through a pump (9) and an exchanger (10) which raise its temperature.

The process of the invention will be understood more clearly in the light of the examples below :

Example 1

Mecazine (methyl ethyl azine) is hydrolysed in a plate column. The water and the mecazine are injected

into the top of the column, and vaporised water is injected into the bottom of the column, as illustrated in Figure 1. The operating conditions are as follows :

- Bottom temperature 178-190°C
- Top pressure 7.5 to 9.7 bar (relative)
- Vaporised water injection T : 180-195°C
- Boiling T : 200°C
  P : 16 bar
- Azine injection 4 t/h
- Total water injection 10.4 t/h
- Vaporised water injection 5 t/h
- Removal of hydrazine 9.1 t/h
  (hydrazine hydrate expressed as HZH 14.6 % - water 85.4 %)
- Boiling
  Recycling flow rate 17.7 t/h
  Consumption of vapour 330 t/h
- Removal of ketone (azeotrope) 5 t/h
  (ketone 4 t/h; water 1 t/h)
- Nitrogen vents 12.5 kg/h

The amount of hydrazine, expressed as hydrazine hydrate, decomposed, measured according to the method described above, is 66.9 kg/hour, i.e. a loss of 4.8 % of the hydrazine formed.

Example 2 - Comparative

The same reaction is carried out (see Figure 2) in an identical column, the only differences being as follows :

- all of the water is injected at the top ;
- the amount of removal for the boiling is 420 t/h and the corresponding consumption of vapour is 21.1 t/h instead of 330 t/h and 17.7 t/h, respectively.

The recovery of nitrogen in the vents is 19.4 kg/h instead of 12.5 kg/h.

The amount of hydrazine, expressed as hydrazine hydrate, decomposed is 104 kg/hour, i.e. 7.2 % of the hydrazine hydrate formed.

The process of the invention makes it possible to reduce the decomposition of hydrazine in the reaction medium by 33 %.

CLAIMS

1. Process for manufacturing hydrazine by hydrolysing an azine, which is carried out in a column fed at the top with azine and water, and from which hydrazine is removed at the bottom and the ketone released is removed at the top, characterized in that the heat required for the reactions and the separation of the various components is partly supplied by means of a boiling vessel and partly by injection, into at least one point of the column, of vaporized water.

2. Process according to Claim 1, characterized in that the vaporized water is injected into the bottom of the column.

3. Process according to either of Claims 1 and 2, characterized in that the amount of water injected in the form of vaporized water represents from 20 to 80 % and preferably from 40 to 60 % of the total water.

4. Process according to one of Claims 1 to 3, characterized in that the vaporized water is at a temperature of between 130 and 220°C and at a relative pressure of between 3 and 18 bar.

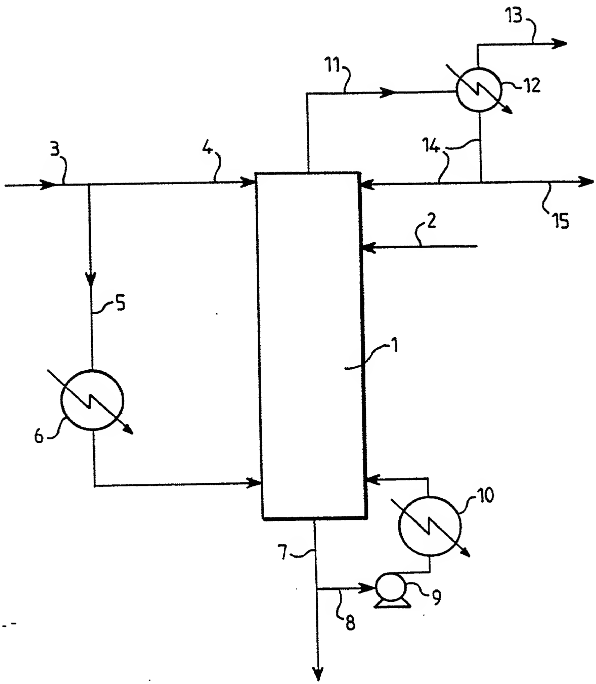


FIG.1

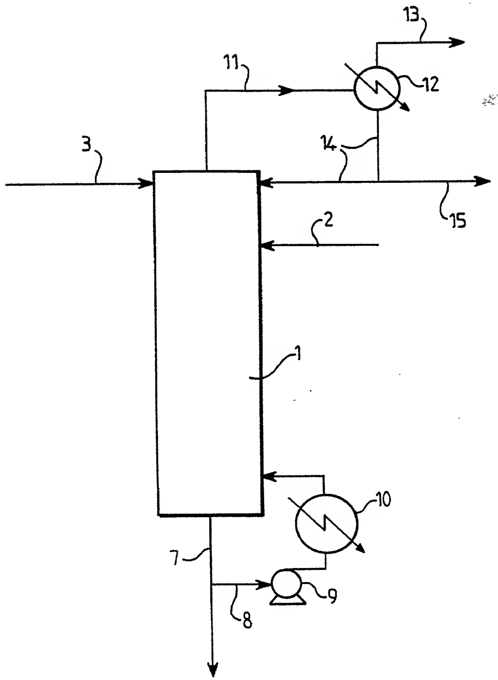


FIG. 2

DECLARATION FOR NON-PROVISIONAL PATENT APPLICATION*

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below at 201 et seq. beneath my name

I believe I am the original, first and sole inventor if only one name is listed at 201 below, or an original, first and joint inventor if plural names are listed at 201 et seq. below, of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR MANUFACTURING HYDRAZINE BY HYDROLYSING AN AZINE

and for which a patent application:
☐ is attached hereto and includes amendment(s) filed on *(if applicable)*
☒ was filed in the United States on June 22, 2001 as Application No. 09/869,207
with amendment(s) filed on *(if applicable)*
☒ was filed as PCT international Application No. PCT/FR99/02786 on November 12, 1999 and was amended under PCT Article 19 on *(if applicable)*

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

☐ I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED PRIOR TO THE FILING DATE OF THE APPLICATION			
APPLICATION NUMBER	COUNTRY	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
WO 00/37357	France	12/22/98	YES ☒ NO ☐
			YES ☐ NO ☐
			YES ☐ NO ☐

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information known to me which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

NON-PROVISIONAL APPLICATION SERIAL NO.	FILING DATE	STATUS		
		PATENTED	PENDING	ABANDONED

* for use only when the application is assigned to a company, partnership or other organization.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

201

FULL NAME OF INVENTOR	LAST NAME: Brenguer	FIRST NAME: Georges	MIDDLE NAME:	
RESIDENCE & CITIZENSHIP	CITY: La Barthe de Neste	STATE OR FOREIGN COUNTRY: France	COUNTRY OF CITIZENSHIP: France	
POST OFFICE ADDRESS	STREET: 23, rue de la Citée	CITY: La Barthe de Neste	STATE OR COUNTRY: France	ZIP CODE: F-65250
	SIGNATURE OF INVENTOR 201		DATE: 06.09.2001.	

202

FULL NAME OF INVENTOR	LAST NAME: Ricard	FIRST NAME: Jean-Philippe	MIDDLE NAME:	
RESIDENCE & CITIZENSHIP	CITY: Pau	STATE OR FOREIGN COUNTRY: France	COUNTRY OF CITIZENSHIP: France	
POST OFFICE ADDRESS	STREET: Avenue de la Fontaine Trespoy Domaine Trespoy	CITY: Pau	STATE OR COUNTRY: France	ZIP CODE: F-64000
	SIGNATURE OF INVENTOR 202		DATE: 11/09/2001	

203

FULL NAME OF INVENTOR	LAST NAME: Vidal	FIRST NAME: Michel	MIDDLE NAME:	
RESIDENCE & CITIZENSHIP	CITY: Lannemezan	STATE OR FOREIGN COUNTRY: France	COUNTRY OF CITIZENSHIP: France	
POST OFFICE ADDRESS	STREET: 379, rue des Bans	CITY: Lannemezan	STATE OR COUNTRY: France	ZIP CODE: 65300
	SIGNATURE OF INVENTOR 203		DATE: 06_09_2001	

204

FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 204		DATE	

205

FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 205		DATE	